

\* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

## DETAILED DESCRIPTION

---

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the water-soluble wrapping which consists of the polyvinyl alcohol system film and this film of a chilled water fast-melting mold in detail about a chilled water fast-melting mold water soluble film and water-soluble wrapping.

[0002]

[Description of the Prior Art]The package of a water soluble film, a detergent, etc., etc. are broadly used as wrapping which presents water solubility from polyvinyl alcohol (henceforth [ PVA ]) being able to carry out [ film ]-izing comparatively easily, and excelling before also in intensity.

[0003]As PVA used for these, the 80 to 90% saponification thing which presents dissolved water in fuel, especially low-temperature-hot-water solubility (low-temperature fusibility) is generally used.

[0004]

[Problem(s) to be Solved by the Invention]However, in the conventional PVA film, even if it is using PVA of the above-mentioned partial saponification thing as the raw material, the performance satisfied not necessarily is not obtained in the use which the solubility in low temperature may be insufficient for, therefore is asked for fastmelt [ in low temperature ].

[0005]Since a saponification reaction advanced by generating of film breakage, such as a crack, or contact with an alkaline substance under low temperature and low humidity, chilled water solubility fell further and there was a problem that it could not be used in a package of an alkaline substance.

[0006]Since an insolubilization thing may generate these PVA films by being exposed to an elevated temperature at the time of heat sealing, in the agricultural-chemicals package, the problem that nozzle plugging occurs at the time of agricultural-chemicals use with a spray

pump is pointed out.

[0007]On the other hand, the applicant has proposed previously the water soluble film using the denaturation polyvinyl alcohol (henceforth "the denaturation PVA") which introduced the anionic group into PVA (Japanese Patent Application No. No. 179064 [ seven to ]), This is dramatically excellent in chilled water fastmelt, and can also prevent deterioration by alkali, and the film breakage under low temperature and low humidity. However, since the hygroscopicity of a film will become large if the denaturation rate is raised in order to improve chilled water fastmelt, there is a problem that humidity must be controlled, in the film of this denaturation PVA, and manufacture of wrapping.

[0008]The purpose of this invention is excellent in the PVA system water soluble film which solved the above-mentioned problem, i.e., cold melting nature, And to temperature and humidity, a change in physical properties is small, and there is no deterioration also in a package of an alkaline substance, and generating of a non-melted object is suppressed to the minimum, and it is in providing the PVA system water soluble film which holds the intensity as wrapping.

[0009]

[Means for Solving the Problem]This invention persons blend wholeheartedly the denaturation PVA which has an anionic group, and PVA which has a saponification degree of a specific range with a fixed rate in view of the above-mentioned problem as a result of examination, It had fastmelt [ to chilled water which easily exceeds anticipation when an obtained film is only mixed ], and also to temperature and humidity, change of physical properties was small, and it found out solving problems, such as film breakage under low temperature and low humidity, and insolubilization by alkali, and resulted in this invention. That is, it is a water soluble film containing denaturation polyvinyl alcohol and the (B) saponification degree 70 - 99-mol% of polyvinyl alcohol which have (A) anionic group.

[0010]

[Embodiment of the Invention]The denaturation PVA which has anionic [ which is the (A) ingredient of this invention first ] is explained in full detail below.

[0011]Although there is no limitation in particular in the degree of polymerization of the anion denaturation PVA used by this invention, 200-8,000 are good and 300-4,000 are preferably good. If a degree of polymerization is less than 200, sufficient film strength will not be obtained, and there is a problem that hygroscopicity becomes large. On the other hand, when a degree of polymerization exceeds 8,000, since aqueous solution viscosity is high, not only fastmelt [ to chilled water ] falls, but it cannot dissolve in high concentration but there is a problem that productivity falls.

[0012]As a denaturation rate of an anionic group, 2.0-40-mol % is good, and it is preferably [ 4.0-30 mol% of ] good. If it is less than [ 2.0 mol % ], while fastmelt [ to chilled water ] will fall,

there is a possibility of causing the film breakage under low temperature and low humidity. The thing exceeding 40-mol % on the other hand is difficult to manufacture.

[0013]Although a carboxyl group, a sulfone group, a phosphate group, etc. are mentioned as a kind of anionic group, a carboxyl group and a sulfone group are desirable in respect of economical efficiency and the ease of carrying out of manufacture.

[0014]What is called the post-denaturation PVA etc. that introduce a carboxyl group into what is called the copolymerization denaturation PVA acquired by saponifying as the carboxyl group denaturation PVA used for this invention, for example after carrying out copolymerization of vinyl acetate, itaconic acid, or the maleic acid, or PVA directly are mentioned.

[0015]As a method of introducing a carboxyl group into PVA by post-denaturation, The method of carrying out piece esterification of the PVA by a maleic anhydride etc., a method to which PVA is made to carry out the substitution reaction of the monochloroacetic acid etc., There are a method to which PVA is made to carry out the Michael addition reaction of the acrylic acid etc., the method of making it hydrolyze selectively or thoroughly, after carrying out the Michael addition reaction of acrylonitrile, the acrylamide, etc. similarly, etc. Among these, conversion is high and the method of hydrolyzing in that the thing of a high denaturation rate is obtained, after carrying out Michael addition of acrylonitrile or the acrylamide is desirable.

[0016]On the other hand as a method of introducing a sulfone group into PVA, For example, vinyl acetate, vinylsulfonic acid, styrene sulfonic acid, allylsulfonic acid, There are a method of making PVA carry out Michael addition of the method of saponifying, after carrying out copolymerization of meta-allylsulfonic acid, the 2-acrylamido-2-methyl propane sulfonic acid (henceforth AMPS), etc., vinylsulfonic acid or its salt, AMPS, or its salt, etc. Among these, conversion is high and the method of making PVA carry out Michael addition of AMPS or its salt in that the thing of high denaturation is obtained is desirable.

[0017]Na salt, K salt, etc. are mentioned as a salt of above-mentioned AMPS.

[0018]The above-mentioned anion-ized agent and two or more sorts of degeneration methods may be used [ in / with a natural thing / manufacture of the anion denaturation PVA ] together.

[0019]Next, PVA of the (B) ingredient is explained in full detail. The saponification degrees of PVA which is the (B) ingredient used for this invention are 70 - 99-mol %, and are 80 - 95-mol % preferably.

[0020]When a saponification degree is less than [ 70 mol % ], chilled water fastmelt falls, and performance is not satisfied in respect of alkali resistance. On the other hand, when exceeding 99-mol %, it is easy to generate the film crack a chilled water fastmelt fall (chilled water insolubilization) and under low temperature and low humidity.

[0021>About a degree of polymerization, 200-8,000 are good for the same reason as the aforementioned (A) ingredient, and 300-4,000 are preferably good.

[0022](A) The mixing ratio of an ingredient and the (B) ingredient can be arbitrarily chosen by

(A):(B) =95-5:5-95% of the weight of within the limits. There is no restriction in particular in a mixing method, and if it is a solid thing, it mixes with a granular material, or each can be used as solution and it can also mix.

[0023]Thus, although a process is not restricted in particular about film-ization of the obtained PVA system constituent, the same process as a publicly known PVA film can be conventionally applied correspondingly.

[0024]For example, after preparing the solution of these PVA(s) system constituent, the cast is carried out to plastic films, such as a belt and PET, and a release paper, or drum lifting, and the casting method to dry is common.

[0025]Although the thickness of the film of this invention can be arbitrarily set up according to the purpose of use, as for the thickness of the film eventually obtained also in which film-ized method, 10-100 micrometers is good in respect of mechanical strength and water fastmelt, and its 10-70 micrometers are more suitably good.

[0026]Since the film of this invention gives pliability, a plasticizer can be used for it if needed. As a plasticizer used for these, the plasticizer used for the usual PVA film can be used, and ethylene glycol, glycerin, diglycerol, and a low-molecular-weight polyethylene glycol (molecular weight: 600 or less) are especially good. Colorant, a release agent, etc. can be blended or applied within limits which do not spoil the main point of this invention. Irregularity working, such as embossing, may be performed in that a blocking preventing process and a fine sight are raised on a film.

[0027]The water-soluble PVA system film of this invention produced by performing it above is a raw material with which has fastmelt [ excellent in chilled water ], an alkaline substance etc. do not deteriorate in a package of medicine, and also it has a raw material and the intensity as wrapping. Therefore, it has the performance which was dramatically excellent as wrapping, such as agricultural chemicals.

[0028]The chilled water fastmelt as used in the field of this invention means the high-speed solubility of the film which water temperature shows in 10 \*\* or less. Although the film of this invention is suitable also as the water transfer film which is a use of the water soluble film currently used conventionally, or various unit wrapping, it can be used for the wrapping in which use was restricted especially conventionally and which requires fastmelt [ in low water temperature ].

[0029]

[Example]Hereafter, an example explains this invention still in detail. Among a sentence, as long as there is no notice especially about a part or %, and a certain thing, it is a weight reference.

[0030](A) 75 copies of example of the example manufacture of manufacture 1 vinyl acetate of an ingredient, 500 copies of methanol, 4.85 copies of itaconic acid, 1.10 copies of NaOH(s),

and 0.3 copy of azobisisobutyronitrile were taught to the separable flask, and it polymerized at 70 °C for 9 hours. The conversion at this time was 81%. After removing unreacted vinyl acetate, 1/10 of the amount of theories of NaOH(s) were added, and it saponified at 40 °C for 5 hours. The degree of polymerization of the acquired carboxy denaturation PVA was 1,200 and saponification degree % of 96.3 mol. When analyzed by NMR, the carboxyl denaturation rate was 3.3-mol %.

[0031]490 copies of PVA(s) (degree-of-polymerization 500 and saponification degree % of 88.2 mol), 200 copies of NaOH(s), 420 copies of 50%-monochloro acetic acid solutions, and 200 copies of isopropyl alcohol were added to the horizontal spindle blender of example of manufacture 24 liter capacity, and it stirred at 60 °C for 8 hours. When it dried after methanol refined the acquired output, and analyzed by colloidal titration, the carboxy denaturation rate was 16.2-mol %.

[0032]440 copies of PVA(s) (degree-of-polymerization 2,500 and saponification degree % of 98.8 mol), 200 copies of 30%-NaOH aqueous solutions, and 484 copies of 50%-aqueous acrylamide solutions were added to the horizontal spindle blender of example of manufacture 34 liter capacity, and it stirred at 60 °C for 8 hours. Subsequently, 100 copies of 50%-NaOH(s) were added and hydrolysis was performed at 90 °C for 1 hour. When the obtained powder was analyzed by NMR, the carboxyl denaturation rate was 29.3-mol %.

[0033]Instead of 484 copies of 450% of example of manufacture-aqueous acrylamide solutions, it carried out by the same method as the example 3 of manufacture except [ all ] having used 250 copies of acrylonitrile. When the obtained powder was analyzed by NMR, the carboxyl denaturation rate was 37.6-mol %.

[0034]440 copies of PVA(s) (degree-of-polymerization 1,700 and saponification degree % of 98.5 mol), 280 copies of 50%-NaOH aqueous solutions, and 828 copies of 50%-AMPS solution were added to the horizontal spindle blender of example of manufacture 54 liter capacity, and it stirred at 80 °C for 7 hours. When the obtained powder was analyzed by NMR, the sulfone group denaturation rate was 14.3-mol %.

[0035]440 copies of PVA(s) (degree-of-polymerization 5,000 and saponification degree % of 98.2 mol), 70 copies of 30%-NaOH aqueous solutions, and 284 copies of 50%-aqueous acrylamide solutions were added to the horizontal spindle blender of example of manufacture 64 liter capacity, and it stirred at 60 °C for 4 hours. Subsequently, 125 copies of 50%-NaOH(s) were added and hydrolysis was performed at 70 °C for 1 hour.

[0036]Subsequently, 460 copies of 50%-AMPS sodium salt solution was added, and it stirred at 80 °C for 4 hours. When the obtained powder was analyzed by NMR, the 17.3-mol % and sulfone group denaturation rate of the carboxyl denaturation rate was 6.5-mol %.

[0037]Examples 1-6, and the comparative example 1-2 (A) ingredient and the (B) ingredient were blended at a rate shown in Table 1, and eight sorts of films for an examination were

prepared by the following method.

[0038]

[Table 1]

	(A) 成分	固形分割合	(B) 成分	固形分割合
実施例 1	製造例 1 の変性 P V A	3 5 部	重合度 2500、けん化度 71.1% の P V A	6 5 部
実施例 2	製造例 2 の変性 P V A	3 0 部	重合度 1700、けん化度 94.3% の P V A	4 0 部
実施例 3	製造例 3 の変性 P V A	7 0 部	重合度 1700、けん化度 88.5% の P V A	3 0 部
実施例 4	製造例 4 の変性 P V A	5 0 部	重合度 4000、けん化度 81.7% の P V A	5 0 部
実施例 5	製造例 5 の変性 P V A	3 5 部	重合度 500、けん化度 85.1% の P V A	5 部
実施例 6	製造例 6 の変性 P V A	5 部	重合度 1700、けん化度 90.2% の P V A	9 5 部
比較例 1	製造例 3 の変性 P V A	3 0 部	重合度 1700、けん化度 65.6% の P V A	7 0 部
比較例 2	—	—	重合度 1700、けん化度 94.3% の P V A	1 0 0 部

[0039]Preparation \*\*\*\* of a film, and the denaturation PVA of the (A) ingredient and PVA of the (B) ingredient are mixed at a desired rate, To the obtained PVA system mixture and this PVA system mixture, 3% of glycerin was dissolved in 80 \*\* water so that it might become the viscosity of 15000 - 25000 mPa-s (BH type viscosity meter, 20 rpm, 25 \*\*). After cooling to a room temperature, it cast on the PET film, and dried at 100 more \*\* after 24-hour neglect for 1 hour, and the 40-micrometer-thick film for an examination was prepared. About the obtained film, system performance testing was carried out by the following method. The result was indicated to Table 2.

[0040]The dissolution rate examination film to water was cut to 1 cm x 1 cm, the seal of + was put by aqueous magic, 500 cc of 10 \*\* water prepared for a 1-l. beaker beforehand, the film was dropped all over the stillness water surface, and time until the seal of + disappears thoroughly was measured. When a film adhered to the round relaxation and beaker side, it measured again. The result was performed by three averages and displayed in the unit (second). Even the water temperature of 5 \*\* was evaluated completely like the above. What is not dissolved in 300 seconds presupposed "it is insoluble."

[0041]The mechanical strength examination film was held to 20 \*\*65%RH for 72 hours, and tensile strength (TB:kg/cm strength) and a pace of expansion (EB:%) were measured according to JISK7127, and tearing strength (TR:kg/cm) was measured according to JIS K7128.

[0042]The generating test examination film of the insolubilization thing was cut to 5 cm x 5 cm, and 200 \*\* was pressed for 1 minute with heat pressing. Then, this film was dissolved in 300-cc tap water, filtration desiccation was carried out and insoluble matter was measured.

[0043]The alkali resistance test examination film was cut to 1 cm x 1 cm, and it put on the petri

dish, and  $\text{Na}_2\text{CO}_3$  was carried from on the film, the film concerned was covered by  $\text{Na}_2\text{CO}_3$ , and the dissolution rate to the water above-mentioned after one-month neglect in 40 °C oven was measured. What is not dissolved in 300 seconds presupposed that it is insoluble.

[0044]The weight change of the film was measured under 25 °C of hygroscopicity, and RH80% of conditions. A part for the balanced water at the time of a weight increment being balancing was computed as moisture absorption, and the following standards estimated.

moisture absorption: -- the time of <20% -- hygroscopic : -- smallness and the time of moisture absorption:20-30% -- the time of moisture absorption:>30% among hygroscopic: --

hygroscopic : size [0045]The film neglected under 0 °C of film breakage and RH20% of conditions for 48 hours was bent, and the existence of the film crack was evaluated.

[0046]The overall evaluation system-performance-testing result was judged synthetically, and it evaluated in five steps.

(It is good) 5->4->3->2->1 (bad)

[0047]

[Table 2]

		水溶解速度/秒		機 械 強 度			不溶化物 の発生	耐アルカリ 試験/10℃	吸湿性	フィム 破 損	総 合 評 価
		10℃	5℃	TE (kg/cm <sup>2</sup> )	EB (%)	TR (kg/cm)	(%)	(秒)			
実 施 例	1	4.3	5.3	3.43	100	3.3	0.1	48	小	無	4
	2	3.5	4.3	3.55	100	3.7	0.0	37	小	無	5
	3	2.2	3.0	3.40	100	3.3	0.0	20	小	無	5
	4	2.8	3.3	3.85	95	4.0	0.0	24	小	無	5
	5	1.6	2.1	2.80	140	2.6	0.0	17	小	無	4
	6	4.8	6.0	3.10	120	3.0	0.2	55	小	無	4
比 較 例	1	不溶	不溶	2.20	190	2.3	—	不溶	中	無	2
	2	不溶	不溶	4.20	80	4.1	—	不溶	小	有	1

[0048]

[Effect of the Invention]The PVA system film of this invention consists of PVA excellent in the anion denaturation PVA, mechanical strength, humidity stability which have the outstanding chilled water fastmelt, alkali resistance, etc., and when both are mixed homogeneously and film-ized, the outstanding performance possesses it according to a synergistic effect. That is, the PVA system film of this invention dissolves promptly also to 1. chilled water.

2. It is hard to deteriorate even if it contacts medicine, such as alkali.

3. It is stable to temperature and humidity, and there are few changes in physical properties.

For example, the film crack under low temperature and low humidity (0 °C, 20%), etc. can be

prevented.

4. The mechanical strength as a film or wrapping is excellent.

It has the feature of \*\*.

[0049]Therefore, when it uses for the PVA system film agricultural-chemicals wrapping of this invention, etc., while being able to prevent plugging of the nozzle of a spray pump, the quality degradation of the wrapping in environment with inferior temperature and humidity conditions according [ or ] to medicine can be controlled.

---

[Translation done.]